

ORGANIC MATTER AND SOIL DYNAMICS

C. BLOOMFIELD

Rothamsted Experimental Station, Harpenden, Herts.

THE SUBJECT-MATTER of pedology is the formation and behaviour of soils, and as such it is basically a field science. However, the subject has now reached a stage at which it is developing from an observational to an experimental science—a normal stage in the development of any scientific discipline.

In the experimental study of a soil process, or indeed of any complex process, the overall process must be separated into its constituent 'unit processes', so that these may be studied in detail and under controlled conditions. This, presumably, is 'Experimental Pedology'.

The first essential in such a study is to identify the motive agent. Humic matter is commonly considered as being responsible for the translocation of sesquioxides in the process of podzolization, but it has been our experience that constituents of undecomposed plant material are far more important mobilizing agents, either as such or as the energy source for microbial action. A broad distinction can be made between the iron-mobilizing properties of herbaceous and other plant types. All kinds of fresh plant material dissolve ferric oxide under non-sterile conditions, but sterile water extracts of herbaceous species are very much less active than similar extracts of tree litter.

Many of the features of podzolization can be explained in terms of the reaction between sterile tree leaf extracts and ferric oxide, and for this reason, as the first stage of the investigation, it seemed logical to confine our attention to this admittedly artificial model.

The activity of tree leaf extracts is correlated with their content of polyphenols, and our results indicate that these are the most important single group of compounds involved in the aseptic solution of iron (Bloomfield, 1957). Schnitzer (1957) considers that acidic polysaccharides are the active agents, but we could not detect any mobilization by purified polysaccharides extracted from aspen leaves (Bloomfield, 1958); MacLean and DeLong (1956) found no correlation between polysaccharide content and iron mobilization.

Sterile water extracts of the leaves, and the barks of some of the thirty or so species tested, dissolve considerable amounts of ferric

EXPERIMENTAL PEDOLOGY

oxide, even at artificially high pH values (7-8) and under aerobic conditions, although the extent of solution is decreased by aeration or by raising the pH of the system.

After reacting with ferric oxide, in the dark and anaerobically, leaf extracts give positive tests for ferrous iron with reagents such as 2,2'-dipyridyl. In the presence of organic matter, this is not proof that the iron was in the ferrous state before dipyridyl was added, but in conjunction with the fact that the net extent of solution is less in the presence of oxygen, it seems reasonable to assume that ferric iron is reduced in the process of mobilization. The total amount of iron dissolved exceeds the amount of ferrous iron determined by dipyridyl, so that the question of the valency state of the balance of the dissolved

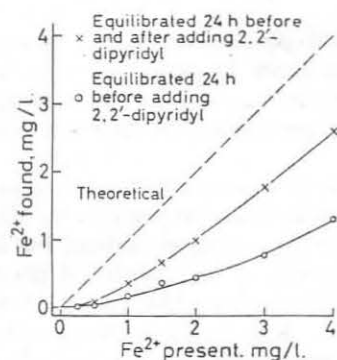


Figure 1. Influence of an aqueous extract of Scots pine needles on reaction of ferrous iron with 2,2'-dipyridyl

iron arises. As the total reducing capacity of an extract greatly exceeds the total solution capacity, it seems probable that this represents ferrous iron in complex form. This can be demonstrated by allowing an extract to react with ferric oxide for several weeks and treating the reaction solution with an excess of a solution of a ferric salt. The dipyridyl-reactive ferrous iron thus produced exceeds the total amount dissolved from the ferric oxide by a considerable factor.

Figure 1 shows that aqueous Scots pine needle extracts form ferrous complexes of a stability comparable with that of ferrous dipyridyl. In this experiment, equal volumes of the extract were treated with increasing amounts of ferrous sulphate; immediate determination of ferrous iron with dipyridyl gave theoretical recoveries, but recoveries were low when the extract was left in contact with the ferrous iron for 24 h before adding dipyridyl. The apparent ferrous contents were intermediate between the two previous values when the mixture was kept in the dark for a further 24 h after adding dipyridyl;

equilibrium between the dipyriddy and extract complexes is thus established slowly, and the value obtained for the apparent ferrous content will depend on the relative concentrations of the various species (Bloomfield, 1953). For this reason we have taken the total iron content of a reaction solution as the only reliable measure of the extent of mobilization.

Reaction solutions are usually dark blue-black; although the coloured compounds are retained on dialysis, considerable quantities of iron pass through the membrane when a leaf extract-ferric oxide reaction solution is dialysed through Cellophane. Dialysates react with 2,2'-dipyridyl, and with some species develop the blue colour of the original reaction solution on exposure to atmospheric oxidation. This suggests that oxidation of organic compounds by ferric iron is involved in the production of the colour of the original solution: the behaviour on dialysis indicates that colloidal properties may develop at the same stage (Bloomfield, 1958).

Expressed as the amount of iron dissolved per unit weight of original leaf material, the net solution of iron decreases with increasing concentration of the extract (Figure 2); this non-stoichiometric

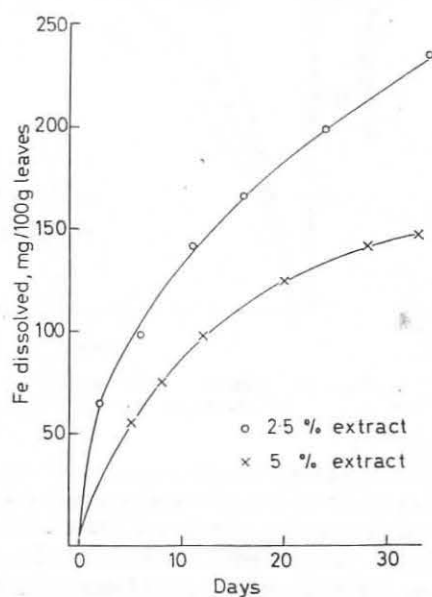


Figure 2. Solution of Fe_2O_3 by rimu leaf extracts; effect of extract concentration
200 ml. extract and 0.1g Fe_2O_3 ; anaerobic

EXPERIMENTAL PEDOLOGY

behaviour appears to be caused by sorption of reaction products on residual ferric oxide. This was demonstrated by passing a reaction solution through a column of ferric oxide-coated quartz sand; iron was retained in the column and could not be removed by washing with water.

Figure 3 shows the effect of varying the amount of ferric oxide present initially.

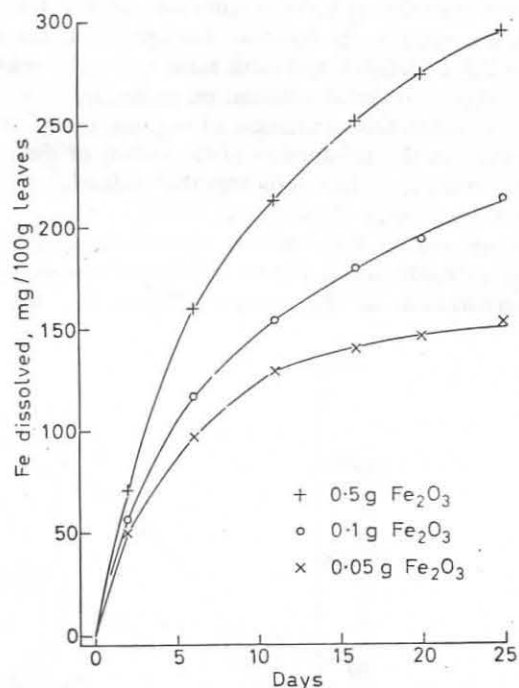


Figure 3. Solution of Fe_2O_3 by 200 ml. 5 per cent rimu leaf extract; effect of amount of ferric oxide

Figure 4 illustrates the effect of successive short treatments with ferric oxide on the iron content of a reaction solution. The solution was prepared by reacting a leaf extract with excess ferric oxide for several days; when treated with additional ferric oxide for 15 min, under nitrogen, the iron content of the solution increased several-fold. This suggests that in the preparation of the solution, sorption of material on the surface of the oxide inhibited its continued solution. Successive treatments with ferric oxide decreased the amount of iron in

solution, giving a curve which is the inverse of the distribution of iron in the profile of a podzol (Bloomfield, 1955b).

This behaviour suggests a possible connection with the deposition of iron and organic matter in the illuvial horizon of a podzol and, indeed, reasonably close reproductions of podzolized profiles have been made in the laboratory by treating columns of ferruginous sand with dilute leaf extracts (Bloomfield, 1955a).

Polyphenols are almost completely removed when leaf extracts are passed slowly through ferric oxide columns, and although under

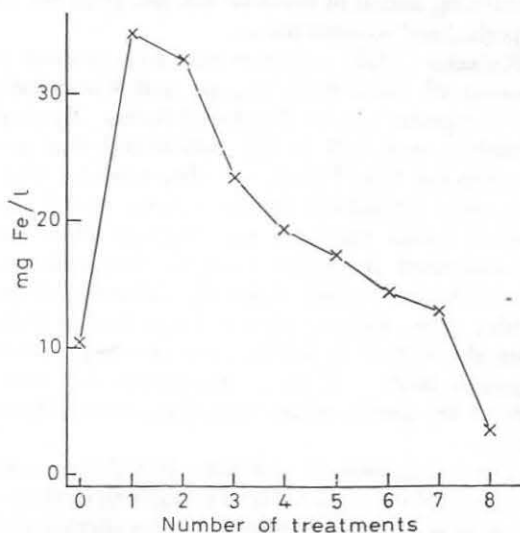


Figure 4. Removal of Fe from a rimu leaf reaction solution by successive treatment with ferric oxide

static conditions the extracts will dissolve comparatively large amounts of ferric oxide, the net removal of iron from the column is very small. For example, after slow passage through a column of kieselguhr-supported ferric oxide, 98 per cent of the polyphenols were removed from an oak leaf extract, and the effluent contained iron equivalent to only 0.5 mg per cent of the original oven-dry leaf material. Under static conditions the corresponding iron figure would be about 200 mg per 100 g of dry leaf. In these experiments the pH values of the effluents usually lie between 7 and 8, compared with values of 4.5–5.0 for the original extracts. Water-extractable polyphenols in leaves falling during autumn have a wide range of molecular weights, and those with larger molecular weights include quite strongly acidic

compounds; presumably the retention of these compounds in the column is responsible for the increased alkalinity of the effluents (Bloomfield, 1962).

Comparatively few species are normally considered as podzol formers, yet all the species tested give leaf extracts that mobilize iron to a greater or lesser extent; in general, broad-leaved species are more reactive than conifers, although podzolization is most often associated with conifers. It follows that unless a completely different mechanism is in fact responsible for podzolization, factors that counteract the mobilizing action of material leached from the litter must operate in unpodzolized wooded areas.

Kubiena (1953) considers that iron podzols develop under acid-tolerant oak woods in N. Europe, and Scheys and collaborators (1954) describe podzols under deciduous cover. By means of pollen analysis, Dimbleby and Gill (1955) established that podzols formed under beech in the New Forest, and they consider that this applies to base-poor areas throughout Britain. Avery (1958) described micropodzols formed under beech in the Chiltern Hills, and Mackney (1961) demonstrated by pollen analysis that podzols at Sutton Park in Warwickshire formed under the influence of the present oak cover. Ashley (priv. comm.) reported a podzol in Northumberland which, from the history of the site, has developed after 30–40 years under Japanese larch. There is thus ample evidence that podzols can be formed by species other than those normally considered as podzol formers.

The palatability of tree litter to soil fauna differs from species to species, and it is reasonable to suppose that there are also differences in the rates of enzymic oxidation of polyphenols in fallen leaves. These factors probably contribute in determining the podzolizing effect of a particular species under given climatic and other conditions.

Enzymic oxidation of polyphenols in fallen leaves decreases the activity of their water extracts, but in some instances our results indicate that the activity may first rise to a maximum before it finally decreases to a quite small value. This appears to be the reason for fallen larch needles being more active than those picked from the tree a few weeks before leaf fall (Bloomfield, 1954).

Lossaint (1959) found that the activities of extracts of aged leaves of alder, hornbeam and two oak species decrease more than those of beech, spruce, fir and pine. It is significant that the species least affected by aging are those more commonly associated with podzolization.

Schnitzer and DeLong (1955) and Lossaint consider that the mobilization of iron by soluble leaf constituents is essentially a process

of colloidal peptization, a view difficult to reconcile with the evidence they adduce for the formation of ferrous compounds. Unless an initial solution stage intervenes, it is necessary to postulate, as does Yarkov (1954), that a solid-phase reduction of ferric oxide is possible under ordinary soil conditions. Schnitzer and DeLong, and Lossaint, apparently worked with aerobic systems, and they were therefore probably dealing with the products of reoxidation; this interpretation of their results is favoured by the fact that Schnitzer found that the ferric to ferrous ratio of mobilized iron was increased by shaking the reaction mixture, presumably in the presence of air (Bloomfield, 1958).

This illustrates the danger involved in making laboratory models for soil processes, and the advantages of studying simplified systems, as, for example, by excluding the possibility of atmospheric reoxidation in the experiments discussed above. Similarly, it may be noted that Lossaint used soil columns in assessing the relative activities of various tree species. Under these conditions, the results would relate only to the net excess of solution over sorption, under conditions permitting the latter to be fully expressed, and which certainly increase the difficulty of detecting the operation of competing reactions.

Hingston (1963) notes that because of the competing influences of solution of iron compounds and precipitation of iron-polyphenol complexes, there is no simple correlation between total polyphenol content and the amount of iron mobilized under aerobic conditions. It might be added that, under anaerobic conditions, resorption phenomena similarly obscure any such correlation.

Lossaint attempted to measure the total reducing capacities of leaf extracts by adding ferric ammonium sulphate and determining the excess ferric iron. Apart from the uncertainty caused by complex formation, we find this procedure unsatisfactory because of the formation of flocculent precipitates when leaf extracts are treated with electrolytes. Probably because of this and associated sorption effects, Lossaint found the specific reducing capacity of an extract to depend upon its concentration in the same way we find the specific capacity to dissolve ferric oxide increases with dilution. The decrease of reducing capacity with increasing pH that Lossaint observed might have resulted from atmospheric oxidation of polyphenols, a process which would be favoured by increased alkalinity.

It has been realized for a long time that nutrients are leached from growing leaves by rainwater (Dalbro, 1955). Schnitzer and DeLong (1954) showed that material able to dissolve and reduce ferric oxide is present in water dripping from the growing canopy, and Davies *et al.* confirmed this observation (1960). As they found little activity in extracts of surface litter, Davies *et al.* consider this to be the most

effective mechanism by which iron-mobilizing plant constituents enter the soil, and they suggest that the activity we observe is derived from material leached from the canopy into the surface litter (Coulson *et al.*, 1960). However, any such tendency could not have operated, as in all our work on deciduous species we have used freshly fallen autumn leaves, which were collected daily. Paper chromatography of water-soluble polyphenols of autumn-fallen leaves, dried under forced draught at 105°C immediately after collection, shows that compounds of large molecular weights constitute by far the greater part of the total phenolic material, and on quantitative grounds must account for most of the activity of the extracts. (This apparently drastic drying treatment is necessary to inactivate enzymes; rapid drying under these conditions appears to cause much less change than slower drying at a lower temperature. Coulson and his co-workers found polyphenols were lost from leaves dried for three days at 25°C before being ground and stored.) The amount of oak leaf polyphenols extracted by 50 per cent methanol decreases when the leaves are exposed in the field in such a way as to prevent attack by soil fauna; after three months' exposure, large-molecular-weight constituents are no longer extracted, and only a very small amount of one compound giving a discrete spot on a paper chromatogram remains. Presumably polyphenols extractable by water would decrease even more rapidly. Coulson and his co-workers may have used litter that had lost its activity in this way. With picked leaves they found most of the phenolic constituents to be small enough to move as discrete spots on paper chromatograms; this probably resulted from their practice of freezing leaves in liquid air immediately after picking, thus preventing oxidation of simple phenolic compounds. As oxidation of polyphenols presumably occurs to some extent during senescence, autumn-fallen leaves are likely to be more relevant to soil processes than those picked during growth.

In our investigations of the properties of leaf extracts we have confined ourselves to sterile systems, and it remains to be seen how far microbial action modifies the process. Despite the artificial conditions of our experiments, the laboratory model agrees quite closely with field observations, so that it may be that there are little more than quantitative differences between sterile and non-sterile systems.

We have not investigated the effect of leaf extracts on the mobilization of trace elements, but Titlyanova and co-workers (1959) found such extracts to be quite effective in desorbing radioactive isotopes of iron, zinc, cobalt and yttrium from soils, but less effective than 0.01 N EDTA. Leaf extracts were more effective than EDTA in desorbing

strontium, but none of the extracts removed caesium. The formation of complexes between zinc and the various leaf extracts was demonstrated by the use of exchange resins.

THE ROLE OF ORGANIC MATTER IN SOIL TRANSFORMATIONS

Many explanations of soil-forming processes of the type considered above postulate that humic matter (or certain fractions isolated from it, i.e. fulvic, crenic, apocrenic acids, etc.) is the causal agent. We have been unable to detect any mobilizing action by humified material, using this term to mean the amorphous, dark-coloured colloidal product of the decomposition of plant material. The results obtained suggest that humus, thus defined, is active as an agent of soil dynamics only insofar as it can act as a source of energy for continued microbial action. This is not to say that humic material does not have important specific properties—for example, its ion-exchange and sequestering properties are important in determining the properties of a soil, and no doubt these properties play an important, but secondary, part in soil development.

It is implicit in many studies of podzols that organic fractions extracted from the *B* horizon are the agents responsible for the translocation of iron, etc. into this horizon. This could be so only if the processes of mobilization and immobilization were purely physical, or of a very simple chemical nature, e.g. the neutralization of an acid. Our results indicate that reduction of ferric iron is involved in the mobilization of ferric oxide, so that even if further chemical and microbiological action were not involved, the organic matter of a podzol *B* horizon is an oxidized and probably polymerized end product of the sequence, and not the causative agent.

Podzols so commonly possess well developed layers of acid mor humus that the presence of such horizons has come to be regarded as a criterion of the podzol, and the process of podzolization is often ascribed to the presence of a mor humus layer. Our results suggest that there is no fundamental reason why there should be any connection between podzolization and the formation of mor, and the fact that the two are so often associated may merely mean that the conditions that favour the development of one also promote the development of the other. It is quite likely, however, that by its action in holding moisture and sealing off the lower horizons, a mor A_0 horizon may favour the development of podzolization.

EXPERIMENTAL PEDOLOGY

REFERENCES

- Avery, B. W. (1958). *J. Soil Sci.* **9**, 210
 Bloomfield, C. (1953). *J. Soil Sci.* **4**, 5; (1954) **5**, 46
 — (1955a). *Chem. & Ind.* 1596
 — (1955b). *J. Soil Sci.* **6**, 284
 — (1957). *J. Sci. Fd Agric.* **8**, 389
 — (1958). *Chem. & Ind.* 259
 — (1962). *Rep. Rothamst. exp. Sta.* 75
 Coulson, C. B., Davies, R. I. and Lewis, D. A. (1960). *J. Soil Sci.* **11**, 30
 Dalbro, S. (1955). *Rep. 16th int. Hort. Cong.* 770
 Davies, R. I., Coulson, C. B. and Lewis, D. A. (1960). *Sci. Proc. R. Dublin Soc.* A **1**, 183
 Dumbleby, G. W. and Gill, J. M. (1955). *Forestry* **28**, 95
 Hingston, F. J. (1963). *Aust. J. Soil Res.* **1**, 63
 Kubiena, W. (1953). *The Soils of Europe*. Murby, London
 Lossaint, P. (1959). *Ann. Agron., Paris* **10**, 369, 493
 Mackney, D. (1961). *J. Soil Sci.* **12**, 23
 MacLean, K. D. and DeLong, W. A. (1956). *Can. J. agric. Sci.* **36**, 267
 Scheys, G., Dudal, R. and Baeyens, L. (1954). *Trans. 5th int. Cong. Soil Sci.* **4**, 274
 Schnitzer, M. (1957). *Chem. & Ind.* 1594
 — and DeLong, W. A. (1954). *Can. J. agric. Sci.* **34**, 542
 — (1955). *Proc. Soil Sci. Soc. Am.* **19**, 360, 363
 Titlyanova, A. A., Tyuryukanov, A. N. and Makhorina, G. I. (1959). *Pochvovedenie* **126**, 1346
 Yarkov, S. P. (1954). *Communs 5th int. Cong. Soil Sci.* 43